DESCRIPTION

STRUCTURE USED IN SEAWATER, COPPER ALLOY WIRE OR BAR FORMING THE STRUCTURE, AND METHOD FOR MANUFACTURING THE COPPER ALLOY WIRE OR BAR

Technical Field

[0001]

The present invention relates to seawater netted structures used under or in contact with seawater, such as fish cultivation nets, seawater intakes of power generating installations or desalinating installations, and seawater strainers of marine engines, to a copper alloy wire or bar used for the netted structure, and to a method for manufacturing the copper alloy wire or bar.

Background Art

[0002]

For example, cultivation nets used for culturing fish, such as tuna, yellowtail, or globefish, are generally made of iron or artificial fiber, such as nylon, polypropylene, or polyethylene (for example, Patent Document 1).

[0003]

Unfortunately, iron cultivation nets (hereinafter referred to as iron nets) and artificial fiber cultivation nets (hereinafter referred to as synthetic nets) easily trap

marine organisms, such as ("acorn shells") and other shellfishes and algae. The marine organisms clog the mesh of the net and thus make it difficult for seawater to pass through the mesh. Consequently, oxygen and nutrients in water cannot be sufficiently supplied to cultivation regions, and thus cultured fish become anorectic. Thus, the productivity and physical strength of the cultured fish are reduced. The cultivation yield is reduced as the resistance to pathogenic bacteria is weakened. Also, parasites, such as gill worms and skin worms, are easily produced. The marine organisms adhering to the net interfere with the behavior of tuna and other migratory fish rubbing against the net. This can adversely affect the growth of cultured fish due to stresses and diseases. Accordingly, it is necessary to frequently remove trapped marine organisms from the net and parasites from the cultured fish. Such work is hard and harsh, and requires extremely high costs.

[0004]

Furthermore, the iron net is liable to be broken in a relatively short time by corrosion of its wires, because iron being the constituent material of the net has a low corrosion resistance to seawater. Even if only a part of a net is broken, cultured fish can escape from the breakage and this results in considerable losses. The iron net therefore needs to be replaced at regular intervals. The

iron net is generally replaced about every two years (or about every year, in some cases). The lifetime of the iron net is thus very short. On the other hand, the synthetic net more easily traps marine organisms, such as shellfishes and algae, than the iron net, and it is accordingly necessary to remove the trapped marine organisms with a frequency of more than or equal to that of the iron net. Although the synthetic net is not corroded by seawater, it inherently has a low shearing strength. Some synthetic nets may result in a shorter lifetime than the iron net depending on circumstances, and may need to be replaced in a shorter time. For replacing a net, cultured fish must be transferred. The replacement of the net not only requires much effort and cost, but also produces adverse effects (for example, stresses) on the cultured fish. The synthetic net also needs to be coated with an antifoulant on a regular basis. The efforts and costs for this work are also high, and the cost for disposing of the waste antifoulant cannot be ignored.

[0005]

Accordingly, it has been proposed that a cultivation net made of copper alloy wires (hereinafter referred to as the copper net) be used instead of the iron net or synthetic net having the above-described disadvantages (for example, Patent Document 2). In use of the copper net, Cu ions

leaching from the wires prevent marine organisms, such as ("acorn shells"), from adhering to the net (this is referred to as "antifouling property") and sterilize or disinfect the culturing seawater region. Hence, it is not necessary to remove organisms adhering to the net. Accordingly, the efforts and costs for removing organisms can be reduced while adverse effects on cultured fish are eliminated. Furthermore, the sterilization or disinfection of culturing regions can prevent diseases of cultured fish and adverse effects of parasites as much as possible, thus allowing the cultured fish to grow healthily at a high speed.

[0006]

Patent Document 1: Japanese Unexamined Patent Application Publication No. 10-337132

Patent Document 2: Japanese Unexamined Patent Application Publication No. 11-140677

Disclosure of Invention
Problems to be Solved by the Invention

[0007]

Cultivation nets are hung under the surface of the sea. If the mechanical strength of the wires of a net is insufficient, the wires may be broken due to their own weight. The cultivation net is swung by waves and wind and rubbed by behaviors of migratory fish. Consequently, the

wires are brought into strong contact (rubbed) with each other and finally worn out. In addition, the cultivation net undergoes repeated collisions with waves. The impacts by the collisions erode the wires of the nets, thereby making the wires thin (so-called erosion-corrosion phenomenon). Furthermore, seawater corrodes metal. The wires are corroded by contact with seawater (this is hereinafter referred to as "seawater corrosion"). At the water line, the rate of seawater corrosion is increased by an oxygen concentration cell or other electrochemical reaction. Therefore, a cultivation net made of wires in which any one of the mechanical strength, the wear resistance, the erosion-corrosion resistance, and the seawater corrosion resistance is insufficient has an unsatisfactory lifetime.

[0008]

Although various materials for copper nets have been proposed, known copper alloys do not satisfy all the requirements for the cultivation net in terms of the mechanical strength, the wear resistance, the erosion-corrosion resistance, and the seawater corrosion resistance. For example, pure copper-based alloys have problems with strength, wear resistance, and erosion-corrosion resistance; Cu-Zn copper alloys have problems with wear resistance, erosion-corrosion resistance, and seawater corrosion

resistance including dezincification corrosion resistance; Cu-Ni copper alloys have problems with wear resistance and erosion-corrosion resistance (and besides material costs). According to experimental results obtained by the present inventors, cultivation nets made of known copper alloys have lifetimes shorter than or equal to those of iron nets. For example, even a net made of naval bronze (JIS C4621, CDA C46400, C46500), which is a copper alloy having a superior seawater resistance, has only substantially the same lifetime as iron nets (lifetime of at most about two years). Since the cultivation net made of a copper alloy uses more expensive material than the iron or synthetic net, the copper net having such a lifetime is money-losing even though it is advantageous in antifouling and disinfection and sterilization. The copper net has not been yet put into practical use because of its poor total cost efficiency including lifetime, although it has an antifouling, a bactericidal, and a sterilizing property superior in cultivation to iron nets and synthetic nets.

[0009]

Accordingly, the object of the present invention is to provide a netted structure used in seawater, such as a fish cultivation net, which has a highly enhanced durability including seawater resistance, with its inherent properties maintained, and to provide a Cu-Zn-Sn copper alloy material

in wire or bar form suitably used for the netted structure.

Means for Solving the Problems

[0010]

According to a first aspect of the present invention, a Cu-Zn-Sn copper alloy material in wire or bar form is provided which forms a seawater netted structure intended for use under or in contact with seawater, such as a fish cultivation net. The copper alloy material is selected from among the following first to sixth compositions.

[0011]

A first copper alloy material has a composition containing: 62 to 91 mass% (preferably 63 to 82 mass%, more preferably 64 to 77 mass%) of Cu; 0.01 to 4 mass% (preferably 0.1 to 3 mass%, more preferably 0.6 to 3 mass%, most preferably 0.8 to 2.5 mass%) of Sn; and the balance being Zn. The compositional value $Y1 = [Cu]-0.5[Sn]$ derived from the Cu content [Cu] and Sn content [Sn] in terms of mass% is 62 to 90 (preferably 62.5 to 81, more preferably 63 to 76, most preferably 64 to 74). The copper apply material has a phase structure including an α phase, a γ phase, and a δ phase, and the total area ratio of the α, γ, and δ phases is 95 to 100% (preferably 98 to 100%, more preferably 99.5 to 100%).

[0012]

A second copper alloy material further contains at least one element X1 selected from the group consisting of As, Sb, Mg, and P, in addition to the composition of the first copper alloy material. More specifically, the second copper alloy material has a composition containing: 62 to 91 mass% (preferably 63 to 82 mass%, more preferably 64 to 77 mass%) of Cu; 0.01 to 4 mass% (preferably 0.1 to 3 mass%, more preferably 0.6 to 3 mass%, most preferably 0.8 to 2.5 mass%) of Sn; at least one element X1 selected from the group consisting of 0.02 to 0.25 mass% (preferably 0.03 to 0.12 mass%) of As, 0.02 to 0.25 mass% (preferably 0.03 to 0.12 mass%) of Sb, 0.001 to 0.2 mass% (preferably 0.002 to 0.15 mass%, more preferably 0.005 to 0.1 mass%) of Mg, and 0.01 to 0.25 mass% (preferably 0.02 to 0.18 mass%, more preferably 0.025 to 0.15 mass%, most preferably 0.035 to 0.12 mass%) of P; and the balance being Zn. The compositional value Y2 = [Cu]-0.5[Sn]-3[P]-0.5[X1] derived from the Cu content [Cu], Sn content [Sn], P content [P], and X1 total content [X1] (except P) in terms of mass% is 62 to 90 (preferably 62.5 to 81, more preferably 63 to 76, most preferably 64 to 74). The copper alloy material has a phase structure including an α phase, a γ phase, and a δ phase, and the total area ratio of the α, γ, and δ phases is 95 to 100% (preferably 98 to 100%, more preferably 99.5 to 100%).
[0013]

A third copper alloy material further contains at least one element X2 selected from the group consisting of Al, Mn, Si, and Ni, in addition to the composition of the first copper alloy material. More specifically, the third copper alloy material has a composition containing: 62 to 91 mass% (preferably 63 to 82 mass%, more preferably 64 to 77 mass%) of Cu; 0.01 to 4 mass% (preferably 0.1 to 3 mass%, more preferably 0.6 to 3 mass%, most preferably 0.8 to 2.5 mass%) of Sn; at least one element X2 selected from the group consisting of 0.02 to 1.5 mass% (preferably 0.05 to 1.2 mass%, more preferably 0.1 to 1 mass%) of Al, 0.05 to 1.5 mass% (preferably 0.2 to 1 mass%) of Mn, 0.02 to 1.9 mass% (preferably 0.1 to 1 mass%) of Si, and 0.005 to 0.5 mass% (preferably 0.005 to 0.1 mass%) of Ni; and the balance being Zn. The compositional value $Y3 = [Cu]-0.5[Sn]-3.5[Si]-1.8[Al]+[Mn]+[Ni]$ derived from the Cu content [Cu], Sn content [Sn], Al content [Al], Mn content [Mn], Si content [Si], and Ni content [Ni] in terms of mass% is 62 to 90 (preferably 62.5 to 81, more preferably 63 to 76, most preferably 64 to 74). The copper alloy material has a phase structure including an α phase, a γ phase, and a δ phase, and the total area ratio of the α, γ, and δ phases is 95 to 100% (preferably 98 to 100%, more preferably 99.5 to 100%).

[0014]

A fourth copper alloy material further contains the

elements X1 and X2 in addition to the composition of the
first copper alloy material. More specifically, the fourth
copper alloy material has a composition containing: 62 to 91
mass% (preferably 63 to 82 mass%, more preferably 64 to 77
mass%) of Cu; 0.01 to 4 mass% (preferably 0.1 to 3 mass%,
more preferably 0.6 to 3 mass%, most preferably 0.8 to 2.5
mass%) of Sn; at least one element X1 selected from the
group consisting of 0.02 to 0.25 mass% (preferably 0.03 to
0.12 mass%) of As, 0.02 to 0.25 mass% (preferably 0.03 to
0.12 mass%) of Sb, 0.001 to 0.2 mass% (preferably 0.002 to
0.15 mass%, more preferably 0.005 to 0.1 mass%) of Mg, and
0.01 to 0.25 mass% (preferably 0.02 to 0.18 mass%, more
preferably 0.025 to 0.15 mass%, most preferably 0.035 to
0.12 mass%) of P; at least one element X2 selected from the
group consisting of 0.02 to 1.5 mass% (preferably 0.05 to
1.2 mass%, more preferably 0.1 to 1 mass%) of Al, 0.05 to
1.5 mass% (preferably 0.2 to 1 mass%) of Mn, 0.02 to 1.9
mass% (preferably 0.1 to 1 mass%) of Si, and 0.005 to 0.5
mass% (preferably 0.005 to 0.1 mass%) of Ni; and the balance
being Zn. The compositional value $Y4 = [Cu]-0.5[Sn]-3[P]-0.5[X1]-3.5[Si]-1.8[Al]+[Mn]+[Ni]$ derived from the Cu
content [Cu], Sn content [Sn], P content [P], total X1
content [X1] (except P), Al content [Al], Mn content [Mn],
Si content [Si], and Ni content [Ni] is 62 to 90 (preferably
62.5 to 81, more preferably 63 to 76, most preferably 64 to

74). The copper alloy material has a phase structure including an α phase, a γ phase, and a δ phase, and the total area ratio of the α, γ, and δ phases is 95 to 100% (preferably 98 to 100%, more preferably 99.5 to 100%).

[0015]

Preferably, the total area ratio of the γ and δ phases in the first to fourth copper alloy materials is 0 to 10% (more preferably 0 to 5%, still more preferably 0 to 3%).

[0016]

A fifth copper alloy material has a composition containing: 62 to 91 mass% (preferably 63 to 82 mass%, more preferably 64 to 77 mass%) of Cu; 0.01 to 4 mass% (preferably 0.1 to 3 mass%, more preferably 0.6 to 3 mass%, most preferably 0.8 to 2.5 mass%) of Sn; 0.0008 to 0.045 mass% (preferably 0.002 to 0.029 mass%, more preferably 0.004 to 0.024 mass%, most preferably 0.006 to 0.019 mass%) of Zr; 0.01 to 0.25 mass% (preferably 0.02 to 0.18 mass%, more preferably 0.025 to 0.15 mass%, most preferably 0.035 to 0.12 mass%) of P; and the balance being Zn. The compositional value Y5 = [Cu]-0.5[Sn]-3[P] derived from the Cu content [Cu], Sn content [Sn], and P content [P] in terms of mass% is 62 to 90 (preferably 62.5 to 81, more preferably 63 to 76, most preferably 64 to 74). The copper alloy material has a phase structure including an α phase, a γ phase, and a δ phase, and the total area ratio of the α, γ,

and δ phases is 95 to 100% (preferably 98 to 100%, more preferably 99.5 to 100%). Also, the average grain size of the copper alloy material is 0.2 mm or less (preferably 0.1 mm or less, optimally 0.06 mm or less) after melt-solidification. The average grain size after melt-solidification mentioned in the fifth copper alloy material and the below-described sixth to eighth copper alloy materials refers to the average of macroscopic and/or microscopic crystal grain sizes after melt-solidification performed by casting or welding the copper alloy material, without deformation processing (extrusion, rolling, etc.) or heat treatment.

[0017]

A sixth copper alloy material further contains at least one element X3 selected from the group consisting of As, Sb, and Mg, in addition to the composition of the fifth copper alloy material. More specifically, the sixth copper alloy material has a composition containing: 62 to 91 mass% (preferably 63 to 82 mass%, more preferably 64 to 77 mass%) of Cu; 0.01 to 4 mass% (preferably 0.1 to 3 mass%, more preferably 0.6 to 3 mass%, most preferably 0.8 to 2.5 mass%) of Sn; 0.0008 to 0.045 mass% (preferably 0.002 to 0.029 mass%, more preferably 0.004 to 0.024 mass%, most preferably 0.006 to 0.019 mass%) of Zr; 0.01 to 0.25 mass% (preferably 0.02 to 0.18 mass%, more preferably 0.025 to 0.15 mass%,

most preferably 0.035 to 0.12 mass%) of P; at least one
element X3 selected from the group consisting of 0.02 to
0.25 mass% (preferably 0.03 to 0.12 mass%) of AS, 0.02 to
0.25 mass% (preferably 0.03 to 0.12 mass%) of Sb, and 0.001
to 0.2 mass% (preferably 0.002 to 0.15 mass%, more
preferably 0.005 to 0.1 mass%) of Mg; and the balance being
Zn. The compositional value Y6 = [Cu]-0.5[Sn]-3[P]-0.5[X3]
derived from the Cu content [Cu], Sn content [Sn], P content
[P], and total X3 content [X3] in terms of mass% is 62 to 90
(preferably 62.5 to 81, more preferably 63 to 76, most
preferably 64 to 74). The copper alloy material has a phase
structure including an α phase, a γ phase, and a δ phase, and
the total area ratio of the α, γ, and δ phases is 95 to 100%
(preferably 98 to 100%, more preferably 99.5 to 100%). The
average grain size after melt-solidification is 0.2 mm or
less (preferably 0.1 mm or less, most preferably 0.06 mm or
less).

[0018]

A seventh copper alloy material further contains at
least one element X4 selected from the group consisting of
Al, Mn, Si, and Ni in addition to the composition of the
fifth copper alloy material. More specifically, the seventh
copper alloy material has a composition containing: 62 to 91
mass% (preferably 63 to 82 mass%, more preferably 64 to 77
mass%) of Cu; 0.01 to 4 mass% (preferably 0.1 to 3 mass%,

more preferably 0.6 to 3 mass%, most preferably 0.8 to 2.5 mass%) of Sn; 0.0008 to 0.045 mass% (preferably 0.002 to 0.029 mass%, more preferably 0.004 to 0.024 mass%, most preferably 0.006 to 0.019 mass%) of Zr; 0.01 to 0.25 mass% (preferably 0.02 to 0.18 mass%, more preferably 0.025 to 0.15 mass%, most preferably 0.035 to 0.12 mass%) of P; at least one element X4 selected from the group consisting of 0.02 to 1.5 mass% (preferably 0.05 to 1.2 mass%, more preferably 0.1 to 1 mass%) of Al, 0.05 to 1.5 mass% (preferably 0.2 to 1 mass%) of Mn, 0.02 to 1.9 mass% (preferably 0.1 to 1 mass%) of Si, and 0.005 to 0.5 mass% (preferably 0.005 to 0.1 mass%) of Ni; and the balance being Zn. The compositional value $Y7 = [Cu]-0.5[Sn]-3[P]-3.5[Si]-1.8[Al]+[Mn]+[Ni]$ derived from the Cu content $[Cu]$, Sn content $[Sn]$, P content $[P]$, Al content $[Al]$, Mn content $[Mn]$, Si content $[Si]$, and Ni content $[Ni]$ in terms of mass% is 62 to 90 (preferably 62.5 to 81, more preferably 63 to 76, most preferably 64 to 74). The copper alloy material has a phase structure including an α phase, a γ phase, and a δ phase, and the total area ratio of the α, γ, and δ phases is 95 to 100% (preferably 98 to 100%, more preferably 99.5 to 100%). Also, the average grain size after melt-solidification is 0.2 mm or less (preferably 0.1 mm or less, most preferably 0.06 mm or less).

[0019]

A eighth copper alloy material further contains the
elements X3 and X4 in addition to the composition of the
fifth copper alloy material. More specifically, the eighth
copper alloy material has a composition containing: 62 to 91
mass% (preferably 63 to 82 mass%, more preferably 64 to 77
mass%) of Cu; 0.01 to 4 mass% (preferably 0.1 to 3 mass%,
more preferably 0.6 to 3 mass%, most preferably 0.8 to 2.5
mass%) of Sn; 0.0008 to 0.045 mass% (preferably 0.002 to
0.029 mass%, more preferably 0.004 to 0.024 mass%, most
preferably 0.006 to 0.019 mass%) of Zr; 0.01 to 0.25 mass%
(preferably 0.02 to 0.18 mass%, more preferably 0.025 to
0.15 mass%, optimally 0.035 to 0.12 mass%) of P; at least
one element X3 selected from the group consisting of 0.02 to
0.25 mass% (preferably 0.03 to 0.12 mass%) of As, 0.02 to
0.25 mass% (preferably 0.03 to 0.12 mass%) of Sb, 0.001 to
0.2 mass% (preferably 0.002 to 0.15 mass%, and more
preferably 0.005 to 0.1 mass%) of Mg; at least one element
X4 selected from the group consisting of 0.02 to 1.5 mass%
(preferably 0.05 to 1.2 mass%, more preferably 0.1 to 1
mass%) of Al, 0.05 to 1.5 mass% (preferably 0.2 to 1 mass%)
of Mn, 0.02 to 1.9 mass% (preferably 0.1 to 1 mass%) of Si,
and 0.005 to 0.5 mass% (preferably 0.005 to 0.1 mass%) of
Ni; and the balance being Zn. The compositional value Y8 =
[Cu]-0.5[Sn]-3[P]-0.5[X3]-3.5[Si]-1.8[Al]+[Mn]+[Ni] derived
from the Cu content [Cu], Sn content [Sn], P content [P],

total X3 content [X3], Al content [Al], Mn content [Mn], Si content [Si], and Ni content [Ni] in terms of mass% is 62 to 90 (preferably 62.5 to 81, more preferably 63 to 76, most preferably 64 to 74). The copper alloy material has a phase structure including an α phase, a γ phase, and a δ phase, and the total area ratio of the α, γ, and δ phases is 95 to 100% (preferably 98 to 100%, more preferably 99.5 to 100%). Also, the average grain size after melt-solidification is 0.2 mm or less (preferably 0.1 mm or less, most preferably 0.06 mm or less).

[0020]

Each of the fifth to eighth copper alloy materials is prepared by adding Zr and P, which are grain-refining elements, to each composition of the first to fourth copper alloy materials. Thus, the crystal grains of the fifth to eighth copper alloy materials are refined after melt-solidification so as to further improve the characteristics that the first to fourth copper alloy materials originally have and so as to ensure a high castability. Specifically, the fifth to eighth copper alloy materials respectively have the same or substantially the same composition (constituted of the same elements in the same proportions except the balance being Zn) as the first to fourth copper alloy materials (referred to as copper alloy materials before improvement for the comparison with the fifth to eighth

copper alloy materials), except for containing Zr and P.
Each of the fifth to eighth copper alloy materials is
modified so that its macroscopic or microscopic average
grain size is reduced by 1/4 or less (preferably 1/10 or
less, more preferably 1/25 or less) after melt-
solidification, by adding Zr and P together. In order to
modify the cooper alloy material more effectively, the Sn
content [Sn], Zr content [Zr], and P content [P] in terms of
mass% of the fifth to eighth copper alloy materials
preferably satisfy Z1=0.5 to 150 (preferably Z1=0.8 to 50,
more preferably Z1=1.5 to 15, most preferably Z1=2.0 to 12),
Z2=1 to 3000 (preferably Z2=15 to 1000, more preferably
Z2=30 to 500, most preferably Z2=40 to 300), and Z3=0.2 to
250 (preferably Z3=3 to 160, more preferably Z3=5 to 90,
most preferably Z3=8 to 60), wherein Z1=[P]/[Zr],
Z2=[Sn]/[Zr], and Z3=[Sn]/[P]. In addition, the total area
ratio of the γ and δ phases in the phase structure is
preferably 0 to 10% (more preferably 0 to 5%, still more
preferably 0 to 3%). Optimally, the γ phase is in a
boundary state where it may be formed or not; hence, it is
most preferable that the area ratio of the γ phase be
enormously close to 0%. Optimally, the β phase is not
produced, or if produced, its area ratio should be limited
to 5% or less. Preferably, the fifth to eighth copper alloy
materials each result in a crystal structure whose dendritic

network is broken after melt-solidification, and more preferably the two-dimensional crystal grain structure is in a circular form or a similar form after melt-solidification. In order to refine the crystal grains during melt-solidification, it is important to take into account the cooling speed during melt-solidification. For example, if the cooling speed is 0.05°C/s or less, the rate of dendrite growth becomes higher than that of crystal nucleation, so that the crystal nucleation is canceled by the dendrite growth. Consequently, the crystal grains cannot be refined effectively. In order to produce fine circular or similar crystal grains, it is preferable that the cooling speed during melt-solidification be taken into account. In general, a preferred cooling speed is 0.1°C/s or more (more preferably 0.3°C/s or more). The crystal grain size, crystal structure, and two-dimensional crystal grain structure after melt-solidification refer to those after melt-solidification performed by casting or welding the fifth to eighth copper alloy materials, without deformation processing, such as extrusion or rolling, or heat treatment.

[0021]

Any of the fifth to eighth copper alloy materials may contain inevitable impurities. If the copper alloy material contains Fe and/or Ni as inevitable impurities (except for the seventh and eighth copper alloy materials containing Ni),

their contents are each preferably 0.5 mass% or less. If
the content of these impurities is high, they consume Zr and
P (which contribute to crystal grain refining), to inhibit
the crystal grain refining, disadvantageously. It is
therefore preferable that if Fe and/or Ni is contained as
impurities, their contents are each limited to 0.5 mass% or
less (more preferably 0.2 mass% or less, still more
preferably 0.1 mass% or less, most preferably 0.05 mass% or
less).

[0022]

The first to fourth copper alloy materials are
generally provided in plastic-processed form prepared by
plastic processing (extrusion or rolling, and physical
deformation processing that may be performed subsequent to
the extrusion or rolling, such as wiredrawing, drawing, or
rolling) in which large casting material (for example,
billet or ingot) obtained by metal mold casting is formed
into wires or bars. For example, such plastic-processed
materials include primary plastic-processed wires or bars
obtained by extruding or rolling a casting material and
secondary plastic-processed wires or bars obtained by
subjecting the primary plastic-processed wires or bars to
wiredrawing, drawing, or rolling. The fifth to eighth
copper alloy materials are provided in combined-processed
wire or bar form prepared by casting, such as horizontal

continuous casting or upward casting (up-casting), or by subsequently subjecting the cast-processed material to plastic processing (physical deformation processing, such as wiredrawing). The combined-processed material is obtained by, for example, wiredrawing, drawing, or rolling of a cast-processed material. In the plastic processing for preparing the plastic-processed material or the combined-processed material, the following cases can be thought of according to the difference between the diameters before and after processing the wires or bars: (1) the same procedure for plastic processing is repeated several times (for example, wiredrawing or drawing is repeated several times); (2) different types of plastic processing are combined (for example, a material is extruded, and subsequently the extruded material is subjected to wiredrawing), and (3) cases (1) and (2) are combined (for example, an extruded material is repeatedly subjected to wiredrawing several times). In any case of (1) to (3), appropriate heat treatment (annealing) is performed once or more before and/or after the plastic processing, as needed. Such heat treatment may be performed in order to enhance the antifouling property or antibiotic properties (bactericidal and sterilizing properties) of the copper alloy material.

[0023]

In the first to eighth copper alloy materials, Cu and

Zn are necessary for controlling leaching of the copper ions from the copper alloy material under seawater, ensuring strength sufficient for cultivation nets or the like, and preventing the material from being worn out by contact with waves and fish and contact with other parts of the material. These effects cannot be sufficiently produced if the Cu content is less than 62 mass%. The corrosion resistance also becomes poor. Also, a Cu content of more than 91 mass% cannot achieve sufficient seawater resistance, and the strength and the wear resistance become poor. In order for Cu and Zn to ensure sufficient strength, corrosion resistance, and seawater resistance, the Cu content should be set at 62 to 91 mass%. For setting the Cu content, the proportions to the other constituent elements must be considered. In particular, the lower limit and upper limit of the Cu content should be set in view of the following considerations, but depending on the ratio of the Sn content to the Zn content. The lower limit should be set so that, first, a more stable corrosion resistance and erosion-corrosion resistance can be ensured and, second, the primary crystal is in an α phase during melt-solidification and involved in peritectic reaction so as to allow grain refining during melt-solidification. The upper limit should be set so that, first, a higher strength and wear resistance are ensured and, second, the copper alloy material has such

a low hot deformation resistance as to be extruded through a small diameter, from the viewpoint of cost reduction, if it is prepared by hot extrusion. Third, the upper limit should be set so as to allow peritectic reaction for further grain refining during melt-solidification. In view of these considerations, the Cu content should be set at 62 to 91 mass%, preferably 63 to 82 mass%, and most preferably 64 to 77 mass%. Zn, as well as Cu and Sn, is one of the primary constituents of the (Cu-Zn-Sn-based) alloy composition of the first to eighth copper alloy materials. The Zn helps the occurrence of a peritectic reaction, which refines the crystal grains of the alloy during melt-solidification, reduces the stacking fault energy of the alloy to enhance the flowability of the molten metal and accelerate the reduction of its melting point in a wire forming step, and enhances the corrosion resistance (particularly erosion-corrosion resistance) and mechanical strength (tensile strength, proof stress, impact strength, wear resistance, fatigue strength, etc.) of the resulting wires. In particularly the fifth to eighth copper alloy materials, Zn also accelerates crystal grain refining during melt-solidification and prevents Zr from being lost by oxidation.

[0024]

In the first to eighth copper alloy materials, Sn is mainly intended to enhance the corrosion resistance (such as

seawater resistance). The addition of 0.01 mass% or more of Sn enhances the corrosion resistance, the erosion-corrosion resistance, the wear resistance, and the strength. However, a Sn content of more than 4 mass% does not produce these effects to an extent according to the content. On the contrary, such a Sn content results in a degraded castability (causing cracks, shrinkage cavities, and porous shrinkage cavities), thus degrading the hot workability and cold workability. For use of the copper alloy material for fish cultivation nets, by setting the Sn content at 0.1 mass% or more, the strength of the alloy material of the cultivation nets can be increased. A higher Sn content not only enhances the seawater resistance and erosion-corrosion resistance of the cultivation net material, but also prevents the wires from being worn out by waves or the like effectively to enhance the wear resistance to rubbing by fish or rubbing against each other. This is because Sn-rich corrosion-resistant coatings are formed over the surfaces of the wires and the coatings prevent fish from coming into direct contact with the wires, and the wires from being worn out by the contact with seawater flowing at a high speed. In addition, Sn expands the range of composition in which peritectic reaction (refining crystal grains effectively during melt-solidification) can occur. As the Sn content is increased, the peritectic reaction can occur in compositions

having a wider range of Cu content in practice. Accordingly, the Sn content is preferably 0.6 mass% or more, and most preferably 0.8 mass% or more. In contrast, a Sn content of more than 4 mass% allows the γ or δ phase, which is a hard phase having a higher Sn content than the parent phase (α phase), to be notably produced at an area ratio of 10% or more, but depending on the Cu and Zn contents. Consequently, the material can become easy to break during wiredrawing, and the γ phase can be selectively corroded to reduce the seawater resistance. If the net repeatedly suffers strong stresses, the net may result in fatigue fracture. Thus, an excessively high Sn content causes Sn to segregate significantly to degrade the hot ductility and the cold workability and ductility, but depending on the Cu and Zn contents. Furthermore, the range of solidification temperature expands according to the increase of the Sn content, and consequently the castability is degraded. In view of these considerations, the Sn content should be set at 0.01 to 4 mass%, preferably 0.1 to 3 mass%, more preferably 0.6 to 3 mass%, and most preferably 0.8 to 2.5 mass% so as to establish an appropriate ratio of the γ phase to the δ phase. In order to form the γ phase and the δ phase at a ratio in the above range and melt and disperse the Sn uniformly as much as possible, it is preferable that the alloy composition be adjusted so that the compositional

value Y9 = 0.06[Cu]-[Sn] derived from the Cu and Sn contents
is 1 to 4.5 (preferably 1.5 to 4.2, more preferably 2 to 3.8,
most preferably 2.5 to 3.5).

[0025]

In the fifth to eighth copper alloy materials, Zr and P
are added in order to refine the crystal grains of the
resulting copper alloy, particularly the crystal grains
after melt-solidification. Although singly used Zr or P can
only slightly reduce the crystal grain size of the alloy, as
well as other common additive elements, a combined use of Zr
and P can refine the crystal grains remarkably effectively.
This effect of refining the crystal grains is exerted when
the Zr content is 0.0008 mass% or more, preferably 0.002
mass% or more, more preferably 0.004 mass% or more, and most
preferably 0.006 mass% or more, and when the P content is
0.01 mass% or more, preferably 0.02 mass% or more, more
preferably 0.025 mass% or more, and most preferably 0.035
mass% or more. However, if the Zr content reaches 0.045
mass% or the P content reaches 0.25 mass%, the effect of
combined use of Zr and P in crystal grain refining is
completely saturated regardless of other constituents and
their contents. Hence, the Zr and the P content capable of
exerting this effect effectively are 0.045 mass% or less and
0.25 mass% or less, respectively. Such low Zr and P
contents set in the above ranges do not inhibit the

characteristics derived from the other constituents of the resulting alloy. On the contrary, such Zr and P contents allow crystal grain refining, so that Sn can be uniformly dispersed without forming a series of regions having a high content of segregated Sn. Consequently, cast cracks can be prevented and healthy cast with a low microporosity can be produced. Furthermore, the workability in cold drawing and cold extraction can be enhanced and, thus, the characteristics of the resulting alloy can be enhanced. In other words, by adding small amounts of Zr and P, the Cu-Zn-Sn-based copper alloys can be modified so as to have a smaller crystal grain size than their corresponding alloys containing the same constituents except Zr and P (like, for example, the alloy of the fifth copper alloy material corresponding to the first copper alloy material, the alloy of the sixth copper alloy material corresponding to the second copper alloy material, the alloy of the seventh copper alloy material corresponding to the third copper alloy material, and the alloy of the eighth copper alloy material corresponding to the fourth copper alloy material) while ensuring characteristics superior or equivalent to their original characteristics.

[0026]

Zr has an extremely high affinity for oxygen. Accordingly, if raw materials are melted in air or if scraps

(waste cultivation nets) are used as the raw materials, Zr is liable to form oxides or sulfides. Addition of an excessive amount of Zr increases the viscosity of molten metal. The molten metal traps oxides or sulfides during casting, and cast defects thus occur which easily result in blowholes or microporosities. In order to prevent this, melting and casting can be performed in a vacuum or a complete inert gas atmosphere. This however limits the versatility of the process and increases the costs of copper alloys containing Zr as a grain-refining element. In view of these considerations, the Zr content is preferably set so as not to form oxides or sulfides. Such a Zr content is preferably 0.0290 mass% or less, more preferably 0.0240 mass% or less, and most preferably 0.0190 mass% or less. A Zr content in these ranges reduces the formation of zirconium oxides or sulfides and thus makes it possible to produce a healthy copper alloy material constituted of fine crystal grains, even if the fifth to eighth copper alloy materials are reused and melted in air.

[0027]

Accordingly, the Zr content should be 0.0008 to 0.045 mass%, preferably 0.002 to 0.029 mass%, more preferably 0.004 to 0.024 mass%, and most preferably 0.006 to 0.019 mass%.

[0028]

In the fifth to eighth copper alloy materials, P is added in combination with Zr, as described above, to refine the crystal grains. P, however, affects the seawater resistance, corrosion resistance, castability, and cold and hot ductility. In view of the effects of P on the seawater resistance, the corrosion resistance, the castability, and the cold and hot ductility in addition to the effect of combined use of P and Zr in refining the crystal grains, the P content should be set at 0.01 to 0.25 mass%, preferably 0.02 to 0.18 mass%, more preferably 0.025 to 0.15 mass%, and most preferably 0.035 to 0.12 mass%.

[0029]

The present invention is also directed to a method for manufacturing copper alloy materials, particularly the fifth to eighth copper alloy materials. In the method, Zr in copper alloy form is added immediately before pouring in a casting step so that addition of oxides or sulfides of Zr can be prevented in this step. In the casting step of the casting material used in the manufacture of the fifth to eighth copper alloy materials, it is preferable that Zr be added in a form of granular or thin-plate intermediate alloy (copper alloy) immediately before pouring so that addition of Zr in form of oxide or sulfide is prevented. Since Zr is easy to oxidize, as described above, it may be advantageous that, in casting, to add Zr immediately before pouring. In

this instance, the Zr is preferably in an intermediate alloy
form of granules (grain size: about 2 to 50 mm) or thin
plate (thickness: about 1 to 10 mm) having a low melting
point close to the melting point of the targeted copper
alloy and containing many types of constituents (for example,
in a form of Cu-Zr or Cu-Zn-Zr alloy containing mainly 0.5
to 65 mass% of Zr, and 0.1 to 5 mass% each of at least one
element selected from the group consisting of P, Mg, Al, Sn,
Mn, and B), because the melting point of Zr is 800 to 1000°C
higher than that of the targeted copper alloy. In
particular, in order to reduce the melting point so that the
Zr can be easily melted, and in order to prevent Zr from
being lost by oxidation, a Cu-Zn-Zr-based alloy containing
0.2 to 35 mass% of Zr and 15 to 50 mass% of Zn (more
preferably 1 to 15 mass% of Zr and 25 to 45 mass% of Zn) is
preferably used. Zr impairs the electrical and thermal
conductivities, which are inherent characteristics of copper
alloys, but depending on the proportion to P used in
combination with Zr. However, if the content of Zr in a
form of non-oxide or non-sulfide is 0.045 mass% or less
(particularly 0.019 mass% or less), the electrical and
thermal conductivities are hardly reduced by addition of Zr.
Even if the electrical or thermal conductivity is reduced,
the degree of the reduction is very small in comparison with
when Zr is not added.

[0030]

In the fifth to eighth copper alloy material, single use of Sn singly does not much enhance the grain-refining effect. However, Sn used in combination with Zr and P notably exerts the grain-refining effect. Sn enhances the mechanical properties (for example, strength), the corrosion resistance, and the wear resistance. Besides, Sn breaks dendrite arms, or expands the possible ranges of contents of Cu and Zn, which are involved in peritectic reaction, to help peritectic reaction effectively. Sn thus helps the granulation or refining of the crystal grains effectively, and this function of Sn is notably exerted particularly in the presence of Zr (and P). The γ phase produced by adding Sn hinders the growth of crystal grains after melt-solidification, thus contributing to the grain refining of the crystal grains. γ Phases are formed from regions having a high Sn content. Since the regions having a high Sn content are uniformly and finely dispersed in the stage of melt-solidification, the resulting γ phases are also finely dispersed, and consequently hinder the growth of α crystal grains at high temperatures after solidification. The fine dispersion of the γ phase leads to a high corrosion resistance and wear resistance. It is therefore preferable that, in order to produce the effect of the combined use of Zr and P in refining the crystal grains of the fifth to

eighth copper alloy materials, the Zr and the P content be set with consideration of their relationship and the relationship with the Sn content. Specifically, their proportions Z1 (=[P]/[Zr]), Z2 (=[Sn]/[Zr]), and Z3 (=[Sn]/[P]) are preferably set in the above ranges. Among these proportions, Z1 or the proportion of P to Zr is important in refining the crystal grains. If the proportion Z1 is in the above range (Z1=0.5 to 150), the rate of crystal nucleation is higher than that of crystal growth during melt-solidification. Consequently, even the grains of a melt-solidified product can be refined to an extent equivalent to the grains of hot-worked material or recrystallized material. In particular, by setting the proportion Z1 of P to Zr at 0.8 to 50, the degree of crystal grain refining can be improved. A Z1 value of 1.5 to 15 further improves the degree of crystal grain refining; and a Z1 value of 2.0 to 12 still further improves the degree.

[0031]

The element X1 (at least one element selected from the group consisting of As, Sb, Mg, and P) contained in the second and fourth copper alloy materials and the element X3 (at least one element selected from the group consisting of As, Sb, and Mg) contained in the sixth and eighth copper alloy materials are mainly intended to enhance the corrosion resistance (particularly dezincification corrosion

resistance). The addition of 0.02 mass% or more of Sb or As enhances the seawater resistance and the corrosion resistance. In order for these elements to produce the effect of enhancing the corrosion resistance notably, Sb or As is added preferably in an amount of 0.03 mass% or more. However, a Sb or As content of more than 0.25 mass% does not produce this effect to an extent according to the content and reduces the ductility (ease of wiredrawing) of the material. In view of the decrease of ductility, the Sb content and the As content each should be set at 0.25 mass% or less. In addition, in view of the hot workability and the cold workability, their contents are each preferably set at 0.12 mass% or less. Hence, the As and the Sb content each should be 0.02 to 0.25 mass%, and preferably 0.03 to 0.12 mass%.

[0032]

The raw materials of the copper alloy often include scraps (waste heat exchanger tubes), and the scraps often contain S (sulfur). In use of S-containing scraps as raw materials of an alloy, Mg being element X1 or X3 enhances the flowability of molten metal in casting, as well as enhancing the corrosion resistance. Mg can remove constituent S by forming MgS, which has a less negative effect than S. Since the MgS does not adversely affect the corrosion resistance even if it remains in the resulting

alloy, Mg can prevent the degradation of the corrosion resistance resulting from the presence of S in the raw material, effectively. Constituent S in the raw material is liable to be present in grain boundaries and consequently may corrode the grain boundaries. The addition of Mg can prevent the grain boundary corrosion effectively. In order to produce such an effect, the Mg content should be set at 0.001 to 0.2 mass%, preferably 0.002 to 0.15 mass%, and more preferably 0.005 to 0.1 mass%. In the sixth and eighth copper alloy materials, the molten metal may have such a high S content as S consumes Zr, disadvantageously. By adding 0.001 mass% or more of Mg to the molten metal before adding Zr, the constituent S in the molten metal is removed by forming MgS. Thus, the above problem does not occur. However, if the Mg content is more than 0.2 mass%, Mg is oxidized, as in the case of Zr, to increase the viscosity in melting. Consequently, for example, trapped oxides may bring about a cast defect. In the case where Mg is used as X3, therefore, the Mg content is set in the above range.

[0033]

P used as X1 contributes to the increase of seawater resistivity and increases the flowability of the molten metal. These effects are exerted at a P content of 0.01 mass% or more, preferably 0.018 mass% or more, more preferably 0.15 mass% or more, and most preferably 0.12

mass% or more. However, an excessive P may adversely affect the cold and hot ductilities and the castability. In view of this, the P content should be set at 0.25 mass% or less, preferably 0.18 mass% or less, more preferably 0.15 mass% or less, and most preferably 0.12 mass% or less. Hence, the content of P used as X1 should be 0.01 to 0.25 mass%, preferably 0.02 to 0.018 mass%, more preferably 0.025 to 0.15 mass%, and most preferably 0.035 to 0.12 mass%, as in the case of the P used as a necessary constituent in the fifth to eighth copper alloy materials.

[0034]

In the third and fourth copper alloy materials or the seventh and eighth copper alloy materials, element X2 or X4, which is at least one element selected from the group consisting of Al, Si, Mn, and Ni, is added in order to mainly enhance the strength, the flowability, the erosion-corrosion resistance at a high flow rate, and the wear resistance. In particular, the addition of the element X2 or X4 is advantageous when the copper alloy material is used as wires or bars forming seawater netted structures (for example, fish cultivation nets). By adding the element X2 or X4, the wear and tear of the wires or bars can be prevented effectively even under harsh conditions (when the cultivation net is placed in an offing whose environmental conditions are strongly influenced by waves, or when the net

is used for cultivation of large, fast migratory fish that
hits the net to give it a large impact, such as yellowtail
or tuna). For example, a seawater netted structure formed
of a large number of wires (particularly fish cultivation
net) can be worn out or torn rapidly by seawater or waves
running at a high speed, by contact with or hit by cultured
fish, or by rubbing of the wires against each other. Al and
Si each form a strong, corrosion-resistant Al-Sn or Si-Sn
coating over the surface of the wires. The coating enhances
the wear resistance of the wires to prevent the wear and
tear of the wires as much as possible. A combination of Mn
and Sn also form a corrosion-resistant coating.
Specifically, Mn can form an intermetallic compound by
combined use with Si and further enhance the wear resistance
of the wires; hence, Mn mainly has the effect of forming an
intermetallic compound preventing the wear and tear of the
wires. X2 enhances the flowability of molten metal in
casting, as well as enhancing the wear resistance. In order
for X2 to produce these effects, 0.02 mass% or more of Al or
Si should be added (for Al, 0.05 mass% or more is preferable
and 0.1 mass% or more is much preferable; for Si, 0.1 mass%
or more is preferable). If Mn is added, the Mn content
should be 0.05 mass% or more (preferably 0.2 mass% or more).
However, if more than 1.5 mass% of Mn or Al is added, the
ductility is degraded to adversely affect wiredrawing. In

particular, when the resulting cultivation net is used under the above-described harsh conditions, the materials of the net can be cracked or broken by repeated bending or the like. In order to prevent the degradation of ductility and the crack or breakage resulting from repeated bending, effectively, the Si content should be 1.9 mass% or less and the Al and Mn contents each should be 1.5 mass% or less (for Al, 1.2 mass% or less is preferable and 1 mass% or less is more preferable; for Si and Mn, 1 mass% or less is preferable). If Al is used as X2 or X4, it can form a dense oxide coating over the surface of the copper alloy by appropriate heat treatment (annealing), thus further enhancing the durability. In this instance, the Al content is preferably set at 0.1 to 1 mass%, and the heat treatment is preferably performed at a low temperature for a long time. Specifically, the heat treatment is preferably performed at a temperature of 400 to 470°C for 30 minutes to 8 hours. The Ni content should be set at 0.005 mass% or more from the viewpoint of enhancing the corrosion resistance. In view of the influence of Ni on the hot workability and the consumption (inhibiting crystal grain refining) by Ni of Zr and P, which are useful in refining crystal grains in the seventh and eighth copper alloy materials, the Ni content is preferably 0.5 mass% or less (more preferably 0.1 mass% or less).

[0035]

In the first to eighth copper alloy materials, in order to ensure the resulting netted structure (for example, a fish cultivation net) has characteristics (seawater resistance, wear resistance, ductility, strength, etc.) sufficient to be used under or in contact with seawater, the alloy material should have the above-described composition and include α, γ, and δ phases at a total area ratio of 95 to 100% (preferably 98 to 100%, more preferably 99.5 to 100%). An excessive γ and/or δ phase easily causes the alloy material to break during wiredrawing, and particularly brings the γ phase into selective corrosion to degrade the seawater resistance. Although the γ phase enhances the wear resistance and the erosion-corrosion resistance and the δ phase enhances the erosion-corrosion resistance, the presence of the γ and/or δ phase degrades the ductility. In order to bring the strength, wear resistance, and ductility into balance without breaking by wiredrawing or degrading the seawater resistance, the alloy material has the above-described composition and, preferably, the total area ratio of the γ and δ phases is set at 0 to 10% (preferably 0 to 5%, more preferably 0 to 3%). The phase structure may be occupied by 95 to 100% of α phase (preferably 98 to 100%, more preferably 99.5 to 100%), containing neither γ nor δ phase (for example, the phase structure is essentially

composed of only the α phase, or the α and β phases),
depending on the process of plastic processing for
manufacturing the first to eighth copper alloy materials.
If the γ phase is present, it is preferable that the γ phase
be fractured (preferably, into elliptical fragments with a
length of 0.2 mm or less) from the viewpoint of minimizing
the selective corrosion by the γ phase and the degradation
of ductility. Since a series of β phase fragments reduces
the seawater resistance, the β phase should not be formed in
view of the seawater resistance. However, the formation of
the β phase enhances the hot workability (particularly
extrusion workability). Accordingly, the content (area
ratio) of the β phase is preferably 5% or less (preferably
2% or less, more preferably 0.5% or less). If the seawater
resistance is particularly important, it is preferable that
the phase structure do not include the β phase. If any of
the first to eighth copper alloy materials has a phase
structure including the γ phase and/or the β phase, the
copper alloy material is preferably subjected to appropriate
heat treatment (for example, annealing at a temperature of
450 to 600°C for 0.5 to 8 hours) to fracture the γ and β
phases into spherical fragments. By fracturing the γ and β
phases into spherical fragments, the negative effect
resulting from the formation of the γ and β phases can be
eliminated as much as possible. In the presence of

fractured spherical γ phase fragments, for example, the degradation of ductility, which results from the formation of the γ phase, is reduced and the wear resistance is enhanced. The heat treatment is performed by, for example, homogenization annealing (heat treatment at a temperature of 450 to 600°C and cooling to 450°C) of the copper alloy material or its intermediate product, and preferably by subsequent finish annealing at a temperature of 400 to 470°C. Since the combined use of Zr and P refines crystal grains to fracture the γ phase into spherical fragments inevitably, the γ phase can be more uniformly dispersed.

[0036]

In order to provide the above-described phase structure in the first to eighth copper alloy materials, the Sn content should be controlled according to the proportions to the Cu and the Zn content. Specifically, the contents of the constituent elements should be set so that the compositional values Y1 to Y8 are each in the range of 62 to 90 (preferably 62.5 to 81, more preferably 63 to 76, most preferably 64 to 74). The lower limits of Y1 to Y8 are set as described above so that the proportions of the main constituents Cu, Sn, and Zn ensure a superior seawater resistance, erosion-corrosion resistance, and wear resistance. In addition, in view of the cold-drawability, ductility, corrosion resistance and castability associated

with the γ and/or δ phase, the upper limits of Y1 to Y8
should be set as described above. In order to ensure these
properties, the Sn content is varied depending on the Cu
content. In the fifth to eighth copper alloy materials, Zr
and P are added mainly for crystal grain refining. If the
first to fourth copper alloy materials, which do not contain
such grain-refining elements, are produced in wire or thin
bar by hot extrusion, it is preferable that the deformation
resistance in the extrusion be reduced in view of cost. In
order to reduce the deformation resistance as much as
possible, it is preferable that the Cu content be set at
63.5 to 68 mass% (more preferably 64 to 67 mass%) and that
the compositions of the alloys be set so that Y1 to Y8
satisfy the above ranges.

[0037]

The fifth to eighth copper alloy materials achieve
refined crystal grains by adding Zr and P, and have an
average grain size of 0.2 mm or less (preferably 0.1 mm or
less, most preferably 0.06 mm or less) after melt-
solidification. The materials can be produced in wire or
bar form by continuous casting, such as upward casting (up-
casting), and the resulting wire or bar can be put into
practical use. Also, the number of steps in the plastic
processing for preparing plastic-processed or combination-
processed wires or bars can be reduced, and thus the

manufacturing costs can be greatly reduced. If the crystal

grains are not refined, repeated heat treatments (including

homogenization annealing) are required to remove the

dendrite structure peculiar to cast metal and segregated Sn

and to fracture the γ phase into spherical fragments. Also,

coarse crystal grains degrade the surface state of the

resulting material. This easily causes cracks during

plastic processing (wiredrawing or drawing) for forming

wires or bars, in association with the segregation of Sn.

Thus, the number of the steps of plastic processing for

preparing targeted plastic-processed wires or bars is

significantly increased. In contrast, if the crystal grains

are refined as described above, homogenization annealing is

not necessary because segregation is microscopic.

Consequently, the number of the steps of plastic processing

and heat treatment for forming plastic-processed products

(particularly wires or thin bars) being the fifth to eighth

copper alloy materials can be greatly reduced. For example,

by applying wiredrawing or drawing once (wiredrawing twice

including finish wiredrawing for adjusting the temper) and

heat treatment (annealing) once to a casting material or a

cast-processed material, the resulting fifth to eighth

copper alloy materials can have high quality and can be used

suitably for cultivation nets or the like. For example, in

the formation of wires by wiredrawing, since crystal grain

refining enhances the ductility and reduces asperities at the surface of the copper alloy material, breakage during wiredrawing can be prevented. For facing (such as healing) of the surface of the copper alloy material, the cutting allowance can be small. In the case where the γ and/or δ phase precipitates, the phase is present in the grain boundary, and the smaller the crystal grains are, the shorter the phase length is. Accordingly, a special step for fracturing the γ and /or δ phase is not required, or if required, the step can be kept at minimum. Thus the number of steps in the manufacturing process can be greatly reduced, and accordingly the manufacturing costs can be reduced as much as possible. It goes without saying that wires or bars from which segregation is not eliminated do not have satisfactory characteristics, including corrosion resistance and mechanical properties.

[0038]

Since the fifth to eighth copper alloy materials achieve refined crystal grains, as described above, the Sn and the Cu content can be increased without segregation of Sn resulting from a high Sn content, or degradation of extrusion workability due to the increase of hot deformation resistance resulting from a high Cu content. Specifically, while a high Sn content of 1 to 1.5 mass% or more promises to increase the corrosion resistance or other properties

greatly, the high content of Sn brings about segregation so significantly as to easily form cracks, shrinkage cavities, blowholes, or microporosities during melt-solidification, and besides cracks during hot working. However, if crystal grains are refined during melt-solidification, these problems do not occur and the Sn content therefore can be increased to further enhance the seawater resistance. A high Cu content (Cu content: 68 mass% or more) increases the hot deformation resistance to degrade the hot workability notably, particularly extrusion workability. However, if the crystal grains are refined, this problem does not occur and the degradation of hot workability can be prevented even if the Cu content is high.

[0039]

In the fifth to eighth copper alloy materials, the addition of Zr and P is performed to refine the crystal grains, but does not impair the inherent characteristics of the copper alloy. The crystal grain refining by addition of Zr and P ensures characteristics superior or equivalent to the original characteristics of the corresponding copper alloy material containing the same constituents except the grain-refining elements Zr and P, as described above. In order to reduce the average grain size after melt-solidification to the above-described level, the ratio Z1 of P to Zr, which are grain-refining elements, and the ratios

of Sn to Zr and Sn to P, namely Z2 and Z3, are set in the above ranges, in addition to setting the Sn content and other contents so that the copper alloy material has a composition and phase structure satisfying the compositional values Y1, Y3, and Y4, as described above.

[0040]

According to a second aspect of the present invention, a netted structure used in seawater is provided which is formed of any one of the first to eighth copper alloy materials and which leads to, for example, practical copper nets having superior characteristics for fish cultivation (antifouling property, bactericidal and sterilizing properties, etc.).

[0041]

The seawater netted structure of the present invention is formed of copper alloy wires or bars being any one of the first to eighth materials. The netted structure is formed of plastic-processed, cast-processed, or combination-processed wires or bars in a wire netting or grid.

[0042]

Preferably, the seawater netted structure of the present invention is made by forming wires being any one of the first to fourth copper alloy materials or the fifth to eighth copper alloy materials into wire netting. Preferably, the netted structure has a rhombically netted form made by

arranging a large number of waved wires in parallel such
that the adjacent wires are entwined with each other at
their curved portions. The seawater netted structure is
mainly used as a fish cultivation net. The cultivation net
has a ring-shaped reinforcing frame along the lower edge of
the net. The reinforcing frame maintains the shape of the
lower edge of the net, and it is preferably spread with
downward tension. By maintaining the shape by the
reinforcing frame and by applying such tension, the wires
can be prevented as much as possible from rubbing against
each other at the entwined portions. The reinforcing frame
is preferably formed by a pipe made of a copper alloy having
the same composition as the material of the net (wires being
any one of the first to eighth copper alloy materials).

[0043]

In addition to the cultivation net made of any one of
the first to fourth or the fifth to eighth copper alloy
materials (wires), the seawater netted structure of the
present invention may be a seawater intake or the like
formed of any one of the bar-shaped first to fourth or fifth
to eighth copper alloy materials (bars) in a grid manner by
welding or the like.

[0044]

If the wire (netting wire) used for the fish
cultivation net or the like is any one of the first to

fourth copper alloy materials (plastic-processed materials), the wire is prepared by, for example, repeatedly drawing and annealing a wire (diameter: 10 to 25 mm) formed by extrusion of a casting material (billet, ingot, or the like) into a diameter of 3 to 4 mm. In this instance, this wiredrawing is repeated several times depending on the difference in diameter between the extruded wire and the netting wire (percentage of wiredrawing). If the netting wire is any one of the fifth to eighth copper alloy materials, the netting wire is formed by, for example, drawing a cast wire (diameter: 5 to 10 mm) formed by horizontal continuous casting or upward casting (up-casting) into a diameter of 3 to 4 mm and subsequently annealing once or twice. The cast-processed wire formed by horizontal continuous casting or upward casting (up-casting) still contains segregated Sn, and accordingly it may not be suitable for cultivation nets. However, it can be suitably used for seawater netted structures other than the cultivation nets.

Advantages

[0045]

The first to eighth copper alloy materials have extremely superior seawater resistance and durability to the known copper alloy materials. In use for a seawater netted structure used under or in contact with seawater, such as a

fish cultivation net, the copper alloy materials can prevent the corrosion and the wear and tear of the netted structure by seawater, waves, and cultured fish as much as possible, thereby increasing the lifetime of the structure. Accordingly, these copper alloy materials can extend the application of the seawater netted structure to the fields where it has not been used for the reason of the total cost including the lifetime of the alloy, using the superior characteristics (antibiotic property, antifouling property, etc.) of the copper alloy to those of other metals effectively.

[0046]

In particular in the fifth to eighth copper alloy materials, the crystal grains are refined after melt-solidification, that is, grain refining in the cast structure is achieved in terms of not only macroscopic structure but also microscopic structure, by adding small amounts of Zr and P. The above characteristics of these copper alloy materials can be improved more than those of not only the known copper alloy material but also the first to fourth copper alloy materials (copper alloy materials before improvement) containing the same constituent elements except Zr or P. Furthermore, since the crystal grains are refined during casting, the castability can be greatly enhanced and the plastic workability of the copper alloy can

be improved. Thus, the fifth to eighth copper alloy materials allow satisfactory plastic processing, such as extrusion or wiredrawing, after casting.

[0047]

In the seawater netted structure, particularly a fish cultivation net, made of any one of the first to eighth copper alloy materials, the durability, which is a fault in the known copper nets, can be greatly enhanced to the extent that the net can be used in practice in view of the total cost without adversely affecting advantages of the known copper nets. By using the fish cultivation net made of any one of the first to eighth copper alloy materials, any type of fish including large migratory fish can be cultured healthily and economically. In particular, for the fish cultivation net or the like made of any one of the fifth to eighth copper alloy materials, the material can be prepared only by about one or two wiredrawing operations (or by a casting process not requiring even wiredrawing, depending on the conditions or application where the seawater netted structure is used) without extrusion. Accordingly, the number of steps for such processing can be reduced without a large casting or extrusion system, and thus manufacturing costs can be greatly reduced.

Brief Description of the Drawings

[0048]

Fig. 1 is a front view of a fish preserve using a fish cultivation net being a seawater netted structure according to the present invention.

Fig. 2 is a transverse sectional view taken along line II-II of Fig. 1.

Fig. 3 is a fragmentary enlarged front view of the cultivation net.

Fig. 4 is a transverse sectional view taken along line IV-IV of Fig. 1.

Reference Numerals

[0049]

1: support frame

2: float

3: fish cultivation net (seawater netted structure)

3a: periphery

3b: bottom

4: reinforcing frame

4a: straight pipe

4b: L-shaped pipe

5: surface of the sea

6: netting wire (wire)

6a: curved portion (entwined portion)

Best Mode for Carrying Out the Invention

[0050]

Fig. 1 is a front view of a fish preserve using a fish cultivation net being a seawater netted structure according to the present invention, and Fig. 2 is a transverse sectional view taken along line II-II of Fig. 1. Fig. 3 is a fragmentary enlarged front view of the cultivation net, and Fig. 4 is a transverse sectional view taken along line IV-IV of Fig. 1.

[0051]

As shown in Fig. 1, the fish preserve includes a support frame 1, a plurality of floats 2 attached to the support frame 1, and a fish cultivation net 3 hanging from the support frame 1. A reinforcing frame 4 is also attached to the lower edge of the cultivation net 3.

[0052]

The support frame 1 is formed of a metal (for example, iron) square bar, plate, pipe, or the like in a square or rectangular frame form. The support frame 1 doubles as a foothold for cultivation work. The inner periphery of the support frame 1 has an attachment with which the upper edge of the cultivation net 3 is held. The floats 2 are made of expanded polystyrene and attached to the bottom surface of the support frame 1 along the upper edge periphery of the cultivation net 3 in a rectangular ring manner. The floats

2 hold the fish preserve in such a manner as to float the support frame 1 on the surface 5 of the sea.

[0053]

The cultivation net 3, which is formed of copper alloy netting wires 6 with a known net forming machine (metal netting machine) used for manufacturing iron nets, includes a square or rectangular tube-like periphery 3a whose upper edge is joined to the attachment provided at the inner periphery of the support frame 1 with wire ropes or the like, and a square or rectangular bottom 3b closing the lower edge, as shown in Figs. 1 and 2. Specifically, the cultivation net 3 has a rhombically netted structure made by arranging a large number of waved netting wires 6 in parallel such that the curved portions 6a of each netting wire 6 are entwined with the curved portions 6a of the adjacent netting wires 6, as shown in Fig. 3. Any one of the first to fourth copper alloy materials (for example, plastic-processed material A in Example 1) or fifth to eighth copper alloy materials (for example, combination-processed material B (or cast-processed material) in Example 2) is used as the netting wire 6. The shape (lengths of the sides of the periphery 3a, dimensions of the mesh S (see Fig. 3), etc.) of the cultivation net 3 is selected according to the installation site, the type of cultured fish, and the culturing conditions.

[0054]

The reinforcing frame 4 has a square or rectangular ring structure formed by connecting four straight pipes 4a with four L-shaped pipes 4b, as shown in Fig. 4, and is attached to the lower edge of the cultivation net 3 in such a manner as to surround the bottom 3b. The pipes 4a and 4b are made of the same copper alloy as the netting wire 6. The connection of the straight pipes 4a to the L-shaped pipes 4b is such that they permit relative displacement to some extent in the direction of their axes so as to be able to follow the deformation of the cultivation net 3 caused by, for example, waves.

[0055]

The reinforcing frame 4 reinforces the lower edge of the cultivation net 3 to maintain its shape. The shape of the cultivation net 3 is thus maintained at both the upper and lower edges by the support frame 1 and the reinforcing frame 4; hence, the whole shape can be maintained appropriately without being largely deformed by waves, large migratory fish, or the like. The reinforcing frame 4 places downward tension on the periphery 3a of the cultivation net 3 due to its own weight. The reinforcing frame 4 thus functions as a tension-applying member (anchor) for reducing the clearances L (see Fig. 3) between the entwined portions 6a of the netting wires 6 of the periphery 3a of the cultivation net 3 to a uniform small size. The weight of

the reinforcing frame 4 is preferably set so as to apply such a tension as the clearance L becomes 0.1 to 10 mm (preferably 0.5 to 5 mm).

[0056]

The rubbing of the netting wires 6 against each other at the entwined portions 6a can be prevented effectively by remaining the shape of the fish cultivation net 3 with the support frame 1 and the reinforcing frame 4 and reducing the clearance L with the tension of the reinforcing frame 4. Thus, the wear and tear resulting from the relative movement of adjacent netting wires 6 can be prevented as much as possible. The reinforcing frame 4 is used as the occasion arises, but may not be used depending on the type of cultured fish or the environment where the cultivation net 3 is used.

EXAMPLES

[0057]

Example 1 prepared plastic-processed materials in wire form (hereinafter collectively referred to as plastic-processed wires A) having compositions shown in Table 1: Nos. 101 to 108, Nos. 201 to 206, Nos. 301 to 305, and Nos. 401 to 405. Wires No. 101 to 108 belong to the first copper alloy material; wires Nos. 201 to 206 belong to the second copper alloy material; wires Nos. 301 to 305 belong to the

third copper alloy material; wires Nos. 401 to 405 belong to the fourth copper alloy material.

[0058]

The plastic-processed wires Nos. 101 to 108, Nos. 201 to 206, Nos. 301 to 305, and Nos. 401 to 405 were each prepared as follows. First, a cylindrical ingot A-1 having the corresponding composition shown in Table 1 was hot extruded into a round bar A-2 of 12 mm in diameter. Specifically, the compositions containing 68 mass% or more of Cu, which have high hot deformation resistances, were formed into cylindrical ingots A-1 with a diameter of 60 mm and a length of 100 mm, and were then hot extruded into round bars A-2 at 850°C. The compositions containing less than 68 mass% of Cu were formed into cylindrical ingots A-1 with a diameter of 100 mm and a length of 150 mm, and were then hot extruded into round bars A-2 at 800°C. Then, the round bars A-2 were each subjected to cold wiredrawing to form a primary processed wire A-3 of 9 mm in diameter. This wiredrawing was performed through the two steps of: drawing a round bar A-2 into an intermediate wire of 10.2 mm in diameter; and further drawing the intermediate wire into a primary processed wire A-3 of 9 mm in diameter. The primary processed wire A-3 was allowed to stand at 550°C for an hour and then subjected to cold wiredrawing to form a secondary processed wire A-4 of 6 mm in diameter. The secondary

processed wire A-4 was further subjected to cold wiredrawing to form a tertiary processed wire A-5 of 4.3 mm in diameter. The tertiary processed wire A-5 was annealed at 480°C for an hour and then subjected to cold wiredrawing. Thus, the plastic-processed wire A of 4 mm in diameter was obtained.

[0059]

Example 2 prepared combination-processed materials in wire form (hereinafter collectively referred to as combination-processed wires B) having compositions shown in Table 2 or 3: Nos. 501 to 528, Nos. 601 to 607, Nos. 701 to 708, and Nos. 801 to 805. Wires Nos. 501 to 528 belong to the fifth copper alloy material; wires Nos. 601 to 607 belong to the sixth copper alloy material; wires No. 701 to No. 708 belong to the seventh copper alloy material; wires Nos. 801 to 805 belong to the eighth copper alloy material.

[0060]

The combination-processed wires Nos. 501 to 528, Nos. 601 to 607, Nos. 701 to 708, and Nos. 801 to 805 were each prepared as follows. First, a casting wire B-1 of 6 mm in diameter having the corresponding composition shown in Table 2 or 3 was subjected to continuous casting at a low speed (1 m/minute) with a casting apparatus including a melting furnace (ingoting ability: 60 kg) equipped with a horizontal continuous casting machine. Molding is continuously performed with graphite while additive elements were added

as needed so as to give a predetermined composition. Then, the casting wire B-1 was subjected to cold wiredrawing to form a primary processed wire B-2 of 4.3 mm in diameter. This wiredrawing was performed through the two steps of: drawing the casting wire B-1 into an intermediate wire of 5 mm in diameter; and further drawing the intermediate wire into the primary processed wire B-2 of 4.3 mm in diameter. The primary processed wire B-2 was annealed at 480°C for an hour and then subjected to cold wiredrawing. Thus, the combination-processed wire B of 4 mm in diameter was obtained.

[0061]

Comparative Example 1 prepared wires Nos. 1001 to 1006 of 4 mm in diameter (hereinafter collectively referred to as first comparative example wires C) having compositions shown in Table 4 in the same manufacturing process as in the case of the plastic-processed wires A of Example 1. The first comparative example wires C were prepared for comparison with the first to fourth copper alloy materials. As for wire No. 1003, a large defect (crack) occurred in the course of forming the primary-processed wire A-3, and thus no intended wire C was obtained.

[0062]

Comparative Example 2 prepared combination-processed wires Nos. 2001 to 2013 and Nos. 2501 to 2505 of 4 mm in

diameter (hereinafter collectively referred to as second comparative example wires D) having compositions shown in Table 5 in the same manufacturing process as in the case of the combination-processed wires B of Example 2. The second comparative example wires D were prepared for comparison with the fifth to eighth copper alloy materials. Wires Nos. 2501 to 2505 contain the same elements as wires Nos. 501 to 505 respectively, except that crystal grain-refining elements Zr and P were not added. As for wires Nos. 2009 and 2011, large defects occurred in the course of forming the primary processed wires B-2. As for wires Nos. 2010, 2012, and 2502 to 2505, large defects occurred in the course of forming the casting wires B-1. Thus, second comparative example wires D for those numbers were not obtained. As for wires Nos. 2001, 2002, 2005, and 2013, although cracks occurred in their primary processed wires B-2, intended second comparative example wires D were obtained because the cracks were not so large.

[0063]

The resulting wires A, B, C, and D were subjected to tension tests and bending tests for inspecting the mechanical properties as follows.

[0064]

The tension test was performed to obtain the tensile strength (N/mm^2), elongation (%), and fatigue strength

(N/mm^2) of the wires A, B, C, and D with an Amsler universal
tester. The results are shown in Tables 6 to 10. On Nos.
1003, 2009, 2010, 2011, 2012, and 2502 to 2505, which did
not achieve intended wires C and D, the tension test and the
following tests were not performed.

[0065]

For the bending test, each of wires A, B, C, and D
extending in the vertical direction was fixed at the
midpoint and was repeatedly subjected to several bending
operations until the curved portion was cracked, and thus
the durability to repetitive deformation was examined. The
single bending operation was performed such that the upper
portion from the fixed portion was bent in a horizontal
direction at a bend radius of 6 mm, then restored to the
vertical state, further bent in the reverse horizontal
direction, and restored to the vertical state again. The
results are shown in Tables 6 to 10.

[0066]

In addition, wires A, B, C, and D were subjected to the
following seawater resistance tests I to IV and the
dezincification corrosion resistance test specified in ISO
6509 to examine the corrosion resistance and the seawater
resistance.

[0067]

In the seawater resistance tests I to IV, erosion-

corrosion test was performed such that a test solution
(30°C) was jetted at a flow rate of 11 m/s onto test pieces
of the wires A, B, C, and D from a nozzle with a bore of 1.9
mm in the direction perpendicular to the axis of the wires.
After a predetermined time T had elapsed, corrosion weight
loss (mg/cm^2) was measured. The test solution was: 3% salt
solution for seawater resistance tests I and II; a mixed
solution of $CuCl_2 \cdot H_2O$ (0.13 g/L) in 3% salt solution for
seawater resistance test III; and 3% salt solution
containing glass beads (5 vol.%) with a average diameter of
0.115 mm for seawater resistance test IV. The corrosion
weight loss was defined by the difference per square
centimeter (mg/cm^2) between the weights of the test piece
before test and after jetting the test solution onto the
test piece for a time T. The jetting time was: 96 hours for
seawater resistance tests I and III; 960 hours for seawater
resistance test II; and 24 hours for seawater resistance
test IV. The results of seawater resistance tests I to IV
are shown in Tables 6 to 10.

[0068]

In the dezincification corrosion resistance test of ISO
6509, test pieces of the wires A, B, C, and D were each
fixed to a phenol resin such that the exposed surfaces of
the test pieces were perpendicular to the direction of
expansion and contraction, and the surfaces of the test

pieces were ground with emery papers of up to #1200. Then, test pieces were ultrasonic-cleaned in pure water, following by drying. The thus obtained corroded test pieces were immersed in 1.0% copper (II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$) solution and allowed to stand at 75°C for 24 hours. Then, the test pieces were taken out of the solution and the maximum depth of dezincification corrosion (μm) was measured. The results are shown in Tables 6 to 10.

[0069]

The phase structures of the wires A, B, C, and D were subjected to image analysis to measure the area ratios (%) of the α, γ, and δ phases. Specifically, a phase structure image taken at a magnification of 200 times by an optical microscope was binarized with an image processing software program "WinROOF" and the area ratio of each phase was determined. The area ratio of each phase was measured in three views and the average was defined as the area ratio of the corresponding phase. The results, which are shown in Tables 1 to 4, suggest that the phase structure described above is required for the characteristics described above.

[0070]

The average grain sizes (μm) of the wires B and D after melt-solidification were measured. Specifically, the cut surface of the casting wire B-1 was etched with nitric acid, and the average grain size of the macroscopic structure

appearing at the etched surface was measured at a magnification of 7.5 times. This measurement was performed in accordance with the comparison method for estimating average grain size of copper elongation products specified in JIS H0501. More specifically, for the crystal grains of about 0.5 mm or more in diameter, the cut surface was etched with nitric acid and observed at a magnification of 7.5 times; for the crystal grains of about less than 0.1 mm in diameter, the cut surface was etched with a mixed solution of hydrogen peroxide solution and ammonia water and observed at a magnification of 75 time with an optical microscope. The results are shown in Tables 7, 8, and 10.

[0071]

As shown in Tables 6 to 10, it has been shown that the first to eighth copper alloy materials, namely, wires A and B, have superior corrosion resistance and seawater resistance to the comparative example wires C and D, and besides, have superior mechanical properties, such as tensile strength, and durability to repetitive deformation. In the fifth to eighth copper alloy materials, the crystal grains are notably refined by adding Zr and P in combination. Consequently, the above characteristics were extremely increased. In particular, the effect of combined use of Zr and P in refining the crystal grains is clearly shown by comparing the average grain sizes of the combination-

processed wires Nos. 501 to 505 with those of the second comparative example wires Nos. 2501 to 2505 containing the same constituent elements except Zr or P.

[0072]

The wire drawability of wires A, B, D, and C was evaluated according to the following criteria. For wires A and C, when the primary processed wire A-3 (diameter: 9 mm) having no crack was obtained from the round bar A-2 (diameter: 12 mm) by a single wiredrawing operation (processing rate: about 44%), the wire drawability was determined to be good; when the primary processed wire A-3 having no crack could not be obtained by the single wiredrawing operation, but it was obtained by the wiredrawing (two operations) of Example 1 or Comparative Example 1, the wire drawability was determined to be ordinary; when the primary processed wire A-3 having no crack could not be obtained by the wiredrawing (two operations) of Example 1 or Comparative Example 1, the wire drawability was determined to be poor. For wires B and D, when the primary processed wire B-2 (diameter: 4.3 mm) having no crack was obtained from the casting wire B-1 (diameter: 6 mm) by a single wiredrawing operation (processing rate: about 49%), the wire drawability was determined to be good; when the primary processed wire B-2 having no crack could not be obtained by the single

wiredrawing operation, but it was obtained by the
wiredrawing (two operations) of Example 2 or Comparative
Example 2, the wire drawability was determined to be
ordinary; when the primary processed wire B-2 having no
crack could not be obtained by the wiredrawing (two
operations) of Example 2 or Comparative Example 2, the wire
drawability was determined to be poor. The results are
shown in Tables 6 to 10. In these tables, the wires having
good drawability are shown as "Good"; the wires having
ordinary wire drawability are shown as "fair"; the wire
having poor wire drawability are shown as "Poor".

[0073]

The castability of wires B and D was evaluated by a
castability test. In the castability test, the casting wire
B-1 was subjected to continuous casting under the same
conditions as in Example 2 or Comparative Example 2 in three
stages at cast speeds of 3 m/minute, 1.8 m/minute, and 1
m/minute. Whether the castability is good or not was
determined depending on the casting speed at which the
casting wire B-1 having no defect was obtained. The results
are shown in Tables 7, 8, and 10. In the tables, when the
casting wire B-1 having no defect was obtained by high-speed
casting at 3 m/minute, the castability was determined to be
excellent and is shown as "Excellent"; when the casting wire
B-1 having no defect could not be obtained by high-speed

casting, but it was obtained by middle-speed casting at 1.8 m/minute, the castability was determined to be good and is shown as "Good"; when the casting wire B-1 having no defect could not be obtained by high-speed casting or middle speed casting, but it was able to be obtained by low-speed casting at 1 m/minute, the castability was determined to be ordinary and is shown as "Fair"; when the casting wire B-1 having no defect could not be obtained even by low-speed casting (1 m/minute), the castability was determined to be poor and is shown as "Poor". The wired whose castability was determined to be poor (shown as "Poor") were not subjected to the castability test, but the castability was evaluated depending on the casting states in the process for making wires B and D in Example 2 or Comparative Example 2. Specifically, when the casting wire B-1 having no defect could not be obtained in the casting step (low-speed casting at 1 m/minute) of the process, the castability was determined to be poor without conducting the evaluation test.

[0074]

As shown in Tables 6 to 10, it has been shown that the first to eighth copper alloy materials, namely, wires A and B, have superior wire drawability to the comparative example wires C and D. It has also been shown that the fifth to eighth copper alloy materials or wires A have not only superior wire drawability but also superior castability due

to refined crystal grains.

[0075]

Example 3 prepared a square tube-like cultivation net 3 (see Figs. 1 to 3) with a side of 9 m and a depth (length in the vertical direction) of 5 m by netting the plastic-processed wire A obtained in Example 1 or the combination-processed wire B obtained in Example 2 into a rhombically netted structure (mesh S: 40 mm). Specifically, plastic-processed wire No. 405 was netted into cultivation net No. 1, and combination-processed wires Nos. 520, 525, and No. 704 were netted into cultivation nets Nos. 2, 3, and 4, respectively, as shown in Table 11.

[0076]

Comparative Example 3 prepared cultivation nets Nos. 5 and No. 6 having the same shape as in Example 3 by respectively netting the first comparative example wires Nos. 1004 and 1005, as shown in Table 11.

[0077]

Fish preserves as shown in Fig. 1 were constructed using cultivation nets Nos. 1 to 6. For each sample number of cultivation nets, two fish preserves (cultivation nets) were each prepared for culturing yellowtail or salmon. The reinforcing frame 4 (see Figs. 1 and 4) of about 2000 kg was attached to each of cultivation nets Nos. 1 to 6 in such a manner that the clearance L at the entwined portions 6a was

about 2 mm on average.

[0078]

Then, migratory fish (yellowtail and salmon) were
cultured using each fish preserve in a practical fish farm.
When a year had elapsed after the start of the cultivation,
the maximum wire thickness loss (mm) of cultivation nets Nos.
1 to 6 was determined. The wire thickness loss was measured
at arbitrarily selected 10 points (measurement points) in
each section of the corner (corner in draft region) of the
periphery 3a in the draft region (region from 10 cm to 30 cm
under the surface of the sea), the region other than the
corner of the periphery 3a in the draft region (periphery in
draft region), the periphery 3a (region of the periphery
lower than the draft region), and the bottom 3b. The
maximum in the obtained values was defined as the maximum
wire thickness loss. The results are shown in Table 11.
The wire thickness loss was calculated by subtracting the
thickness of each measurement point after a year from the
initial thickness (4 mm) of the measurement point.

[0079]

As clearly shown in Table 11, cultivation nets Nos. 1
to 4 of Example 3 exhibited a much lower wire thickness loss
at each measurement point than cultivation nets Nos. 5 and 6
of Comparative Example 3, in spite of a short period of
testing time (one year). Thus, it has been shown that

cultivation nets of Example 3 have superior durability. In addition, the adhesion of marine organisms, such as ("acorn shells"), to cultivation nets Nos. 1 to 6 was hardly found even after a year had elapsed.

[0080]

Table 1

Wire No.	Alloy composition													Phase structure	
	Constituent element (mass%)											Compositional value		Area ratio (%)	
	Cu	Zn	P	Sn	Al	As	Sb	Mn	Si	Ni	Mg	Y1 to Y8	Y9	α+γ+δ	γ+δ
101	81.5	17.7		0.8								81.1	4.1	100	0
102	90.1	8.5		1.4								89.4	4.0	100	0
103	66.2	32.5		1.3								65.6	2.7	100	2.0
104	65.3	33.6		1.1								64.8	2.8	99.0	1.0
105	66.4	32.6	0.05	1.0								65.8	3.0	100	0.1
106	64.9	34.1	0.10	0.9								64.2	3.0	100	0.5
107	65.0	33.1	0.10	1.8								63.8	2.1	100	7.0
108	65.0	33.4	0.06	1.5								64.1	2.4	100	4.5
201	62.6	36.5		0.8			0.08					62.2	3.0	98.0	0.5
202	63.4	36.0		0.5			0.07					63.1	3.3	99.5	0
203	64.3	34.4		1.2			0.08					63.7	2.7	100	3.5
204	65.5	33.7		0.8		0.04						65.1	3.1	100	0
205	65.5	33.7		0.8							0.02	65.1	3.1	100	0
206	65.3	33.6		1.0		0.10	0.03					64.7	2.9	100	0.5
301	66.0	31.9		1.1				0.7	0.3			65.8	2.9	100	2.0
302	66.5	32.2		1.1					0.2			65.3	2.9	100	1.5
303	65.5	33.4		1.0	0.2							64.7	2.9	100	1.0
304	64.2	33.5		0.9				1.1	0.3			64.9	3.0	100	0
305	67.4	30.7	0.05	1.2	0.7							65.4	2.8	100	1.0
401	66.8	31.7		1.0	0.4		0.07					65.5	3.0	100	0
402	69.1	28.4	0.04	1.0	1.4							66.0	3.1	100	0
403	70.5	26.9		1.3		0.08	0.03		1.2			65.6	2.9	100	4.0
404	66.8	31.7		1.0			0.06		0.4		0.05	64.9	3.0	100	0.5
405	65.8	33.0		1.1			0.06			0.03		65.3	2.8	100	0.3

Example 1

[0081]

Table 2

| Wire No. | Alloy composition | | | | | | | | | | | Phase structure | |
| | Constituent element (mass%) | | | | | | Compositional value | | content ratio | | | Area ratio (%) | |
	Cu	Zn	Zr	P	Sn	impurity	Y1 to Y8	Y9	Z1	Z2	Z3	α+γ+δ	γ+δ
501	68.8	29.9	0.0080	0.060	1.20		68.0	2.9	7.5	150.0	20.0	100	0.5
502	72.6	25.9	0.0090	0.070	1.40		71.7	3.0	7.8	155.6	20.0	100	0
503	75.8	22.1	0.0090	0.050	2.00		74.7	2.5	5.6	222.2	40.0	100	0.3
504	80.5	17.0	0.0150	0.080	2.40		79.1	2.4	5.3	160.0	30.0	100	0
505	90.2	6.2	0.0230	0.090	3.50		88.2	1.9	3.9	152.2	38.9	100	0
506	66.2	32.7	0.0053	0.060	1.00		65.5	3.0	11.3	188.7	16.7	100	0
507	66.0	32.9	0.0015	0.060	1.00		65.3	3.0	40.0	666.7	16.7	100	0.3
508	66.5	32.3	0.0090	0.045	1.10		65.8	2.9	5.0	122.2	24.4	100	0
509	66.8	32.0	0.0120	0.070	1.10		66.0	2.9	5.8	91.7	15.7	100	0
510	66.3	32.6	0.0270	0.060	1.00		65.6	3.0	2.2	37.0	16.7	100	0
511	66.3	32.6	0.0380	0.080	1.00		65.6	3.0	2.1	26.3	12.5	100	0
512	74.1	24.6	0.0180	0.070	1.20		73.3	3.2	3.9	66.7	17.1	100	0
513	63.2	36.0	0.0150	0.060	0.70		62.7	3.1	4.0	46.7	11.7	99.0	0.5
514	62.7	36.6	0.0160	0.060	0.60		62.2	3.2	3.8	37.5	10.0	97.5	1.0
515	66.0	33.9	0.0120	0.050	0.07		65.8	3.9	4.2	5.8	1.4	100	0
516	66.5	33.0	0.0090	0.060	0.45		66.1	3.5	6.7	50.0	7.5	100	0
517	66.0	33.2	0.0140	0.050	0.70		65.5	3.3	3.6	50.0	14.0	100	0
518	76.0	20.5	0.0090	0.050	3.40		74.2	1.2	5.6	377.8	68.0	100	4.5
519	68.8	29.8	0.0180	0.180	1.20		67.7	2.9	10.0	66.7	6.7	100	0.5
520	73.0	25.6	0.0090	0.045	1.30		72.2	3.1	5.0	144.4	28.9	100	0
521	73.5	24.9	0.0130	0.060	1.50		72.6	2.9	4.6	115.4	25.0	100	0.5
522	67.5	30.4	0.0090	0.070	2.00		66.3	2.1	7.8	222.2	28.6	100	8.0
523	66.5	32.0	0.0080	0.080	1.40		65.6	2.6	10.0	175.0	17.5	100	4.5
524	72.2	26.4	0.0150	0.070	1.20	Fe: 0.07	71.5	3.1	4.7	80.0	17.1	100	0

Example 2

[0082]

Table 3

| Wire No. | Alloy composition | | | | | | | | | | | | | | | | | | | Phase structure | |
| | Constituent element (mass%) | | | | | | | | | | | | | Compositional value | | | content ratio | | | Area ratio (%) | |
	Cu	Zn	Zr	P	Sn	Al	As	Sb	Mn	Si	Ni	Mg	impurity	Y1 to Y8	Y9	Z1	Z2	Z3	α+γ+δ	γ+δ
525	72.0	26.7	0.015	0.070	1.2								Fe: 0.03	71.2	3.1	4.7	80.0	17.1	100	0
526	71.0	27.8	0.015	0.070	1.1								Ni: 0.03	70.3	3.2	4.7	73.3	15.7	100	0
527	66.0	32.9	0.035	0.022	1.0									65.4	3.0	0.6	28.6	45.5	100	0
528	66.0	32.8	0.004	0.170	1.0									65.0	3.0	42.5	250.0	5.9	100	0
601	66.0	32.9	0.016	0.015	1.0			0.02						65.4	3.0	0.9	62.5	66.7	100	0.3
602	65.8	33.1	0.009	0.060	0.9		0.10							65.1	3.0	6.7	100.0	15.0	100	0
603	66.5	32.3	0.013	0.028	1.1			0.02						65.9	2.9	2.2	84.6	39.3	100	0
604	66.0	32.8	0.009	0.070	1.1			0.06						65.2	2.9	7.8	122.2	15.7	100	1.0
605	66.2	32.8	0.009	0.120	0.8							0.110		65.4	3.2	13.3	88.9	6.7	100	0
606	72.8	25.7	0.013	0.090	1.4		0.04							71.8	3.0	6.9	107.7	15.6	100	0
607	74.2	24.5	0.019	0.060	1.2							0.008		73.4	3.3	3.2	63.2	20.0	100	0
701	80.3	17.1	0.016	0.070	2.4	0.14								78.6	2.4	4.4	150.0	34.3	100	0.5
702	68.0	30.7	0.009	0.080	1.1					0.15				66.7	3.0	8.9	122.2	13.8	100	0
703	67.2	30.7	0.015	0.050	1.0				0.70	0.35				66.7	3.0	3.3	66.7	20.0	100	0
704	72.5	25.8	0.009	0.060	1.3	0.31								71.1	3.1	6.7	144.4	21.7	100	0
705	68.4	29.8	0.012	0.070	1.2	0.52								66.7	2.9	5.8	100.0	17.1	100	0
706	65.5	31.9	0.010	0.050	0.9				1.20	0.40				65.9	3.0	5.0	90.0	18.0	100	0.3
707	74.0	24.5	0.015	0.080	1.2				0.18	0.07				73.3	3.2	5.3	80.0	15.0	100	0
708	71.5	27.0	0.015	0.080	1.2						0.17			70.9	3.1	5.3	80.0	15.0	100	0
801	67.3	31.3	0.009	0.060	1.2	0.08		0.03						66.4	2.8	6.7	133.3	20.0	100	1.5
802	67.4	31.3	0.012	0.070	1.0	0.20	0.06							66.3	3.0	5.8	83.3	14.3	100	0
803	69.5	28.2	0.009	0.050	1.0	1.20								66.7	3.2	5.6	111.1	20.0	100	0
804	72.0	25.6	0.011	0.080	1.1		0.05	0.03		1.10		0.050		67.3	3.2	7.3	100.0	13.8	100	0
805	67.0	31.7	0.012	0.060	1.0			0.06		0.20				65.6	3.0	5.0	83.3	16.7	100	0

Example 2

[0083]

Table 4

	Wire No.	Alloy composition							Phase structure	
		Constituent element (mass%)					Compositional value		Area ratio (%)	
		Cu	Zn	P	Sn	Sb	Y1 to Y8	Y9	α+γ+δ	γ+δ
Comparative example 1	1001	61.4	37.6		0.900	0.06	60.9	2.8	94.0	1.0
	1002	91.8	7.2		0.900	0.08	91.3	4.6	100	0
	1003	65.5	32.0	0.05	2.500		64.1	1.4	100	12.0
	1004	79.8	20.2		0.005		79.8	4.8	100	0
	1005	65.1	34.9		0.007		65.1	3.9	100	0
	1006	65.2	34.8		0.005	0.01	65.2	3.9	100	0

[0084]

Table 5

Wire No.	Alloy composition													Phase structure	
	Constituent element (mass%)								Compositional value		content ratio			Area ratio (%)	
	Cu	Zn	Zr	P	Sn	Sb	Ni	impurity	Y1 to Y8	Y9	Z1	Z2	Z3	α+γ+δ	γ+δ
2001	65.5	33.4	0.0004	0.060	1.000				64.8	2.9	150.0	2500.0	16.7	99.7	1.0
2002	66.0	33.0	0.0180	0.008	1.000	0.02			65.5	3.0	0.4	55.6	125.0	99.8	0
2003	65.7	33.1	0.0750	0.120	1.000				64.8	2.9	1.6	13.3	8.3	100	1.0
2004	62.0	37.2	0.0160	0.060	0.700				61.5	3.0	3.8	43.8	11.7	96.0	1.0
2005	61.2	38.0	0.0150	0.070	0.700				60.6	3.0	4.7	46.7	10.0	92.0	2.0
2006	64.8	35.1	0.0150	0.060	0.005				64.6	3.9	4.0	0.3	0.1	100	0
2007	91.5	5.6	0.0180	0.100	2.800				89.8	2.7	5.6	155.6	28.0	100	0
2008	90.6	8.8	0.0150	0.060	0.500				90.2	4.9	4.0	33.3	8.3	100	0
2009	75.8	19.8	0.0090	0.050	4.300				73.5	0.2	5.6	477.8	86.0	100	9.0
2010	68.8	29.7	0.0180	0.280	1.200				67.4	2.9	15.6	66.7	4.3	100	1.0
2011	68.0	29.3	0.0090	0.050	2.600				66.6	1.5	5.6	288.9	52.0	100	13.0
2012	73.6	24.5	0.0150	0.070	1.200		0.6		73.7	3.2	4.7	80.0	17.1	100	0
2013	70.8	27.4	0.0150	0.080	1.200			Fe: 0.55	70.8	3.0	5.3	80.0	15.0	100	0
Comparative example 2 2501	68.8	29.9		0.060	1.200				68.0	2.9				100	0.5
2502	72.6	25.9		0.070	1.400				71.7	3.0				100	0
2503	75.8	22.2			2.000				74.8	2.5				100	0.1
2504	80.5	17.0		0.080	2.400				79.1	2.4				100	0
2505	90.2	6.2		0.090	3.500				88.2	1.9				100	0

[0085]

Table 6

wire No.	maximum depth of corrosion (μm)	corrosion weight loss (mg/cm²) erosion-corrosion test				wire drawability	tensile strength (N/mm²)	elongation (%)	fatigue strength (N/mm²)	number of bending sequences
		I	II	III	IV					
101	20	25	140	65	310		372	17	152	>5
102	≤10	22	114	68	350		355	14	148	>5
103	90	27	153	85	275		457	18	168	>5
104	130	29	180	92	335		445	20	174	>5
105	≤10	23	108	60	246	Good	436	22	170	>5
106	20	26	110	68	273		440	22	168	>5
107	150	34	189	105	335	Fair	479	12		2
108	40	26	118	65	256	Fair	468	14		3
201	170	35	202	113	348		450	15		3
202	90	28	145	79	313		437	21		5
203	40	25	118	65	275	Good	456	17		4
204	≤10	22	95	60	230	Good	431	23	174	>5
205	70	32	145	90	325		425	24	165	>5
206	≤10	23	103	65	220	Good	439	22	165	>5
301	20	27	112	65	195		483	14		3
302	≤10	24	110	63	220		440	19		5
303	≤10	26	112	66	245		437	21	168	>5
304	30	27	128	69	160		525	14	188	3
305	≤10	24	102	60	210		475	19	180	>5
401	≤10	23	108	60	213		446	22	174	>5
402	≤10	23	103	62	188		505	17	185	4
403	35	26	120	70	190		508	16	185	3
404	≤10	27	112	68	210		453	21	165	>5
405	≤10	24	104	63	218		435	22	172	>5

Example 1

[0086]

Table 7

	Wire No.	Average grain size (μm)	Maximum depth of corrosion (μm)	Corrosion weight loss (mg/cm²) Erosion-corrosion test				Castability	Wire drawability	Tensile strength (N/mm²)	Elongation (%)	Fatigue strength (N/mm²)	Number of bending sequences
				I	II	III	IV						
	501	30	≤10	21	98	58	205	Excellent	Good	445	21	177	>5
	502	25	≤10	19	93	55	192	Excellent	Good	438	22	174	>5
	503	35	≤10	20	95	54	194	Excellent	Good	431	22	170	>5
	504	65	≤10	20	94	58	228	Good	Good	430	20	166	>5
	505	95	≤10	21	89	56	277	Good	Good	418	19	155	>5
	506	50	≤10	24	116	66	245	Excellent	Good	436	23	168	>5
	507	120	≤10	25	123	72	266	Good	Good	418	20	153	>5
	508	30	≤10	24	105	61	228	Excellent	Good	446	23	180	>5
	509	25	≤10	23	101	60	215	Excellent	Good	438	23	178	>5
	510	50	≤10	24	107	62	235	Excellent	Good	438	22	172	>5
	511	90	≤10	23	108	65	233	Excellent	Good	435	21	170	>5
	512	30	≤10	23	102	62	226	Excellent	Good	420	24	175	>5
Example 2	513	40	120	29	161	89	328			437	22	155	5
	514	55	190	34	211	115	372			440	19	153	4
	515	40	≤10	28	169	81	392			413	25	151	>5
	516	35	≤10	27	139	70	301			420	25	160	>5
	517	30	≤10	26	115	72	278			425	23	165	>5
	518	35	30	22	99	58	183	Fair	Fair	448	12	167	3
	519	90	≤10	21	98	59	196			435	17		4
	520	35	≤10	19	93	55	192	Excellent	Good	438	22	174	>5
	521	25	≤10	19	89	53	182	Excellent	Good	428	20	180	>5
	522	30	100	29	132	81	280		Fair	451	11		3
	523	25	40	25	111	65	213		Fair	462	14		3
	524	120	≤10	22	103	65	218	Excellent		435	19	165	>5

[0087]

Table 8

Wire No.	Average grain size (μm)	Maximum depth of corrosion (μm)	Corrosion weight loss (mg/cm²) Erosion-corrosion test				Castability	Wire drawability	Tensile strength (N/mm²)	Elongation (%)	Fatigue strength (N/mm²)	Number of bending sequences
			I	II	III	IV						
525	40	≤10	22	102	61	215	Excellent		442	21	170	>5
526	35	≤10	21	100	59	205	Excellent	Good	438	22	168	>5
527	180	40	26	128	74	285			422	21	150	>5
528	200	20	23	110	67	235			430	17	160	4
601	120	40	26	135	74	285	Good	Fair	422	18	150	4
602	25	≤10	23	107	66	243			435	25	173	>5
603	70	20	23	110	67	235	Excellent	Good	443	21	163	>5
604	30	≤10	24	108	62	222			442	23	175	>5
605	25	≤10	24	107	69	228	Excellent	Good	430	24	168	>5
606	30	≤10	18	88	54	190			442	23		>5
607	40	≤10	20	90	55	194			428	22		>5
701	70	≤10	19	90	57	208	Excellent	Good	433	21	160	>5
702	30	≤10	23	102	62	200			446	22		>5
703	35	≤10	24	108	66	172			485	18	185	4
704	25	≤10	19	88	51	172	Excellent	Good	446	23	175	>5
705	25	≤10	21	94	55	180	Excellent	Good	455	23	185	>5
706	40	≤10	24	110	67	145			478	18	190	4
707	35	≤10	19	104	59	198			452	20	180	>5
708	180	≤10	23	108	67	230	Good	Fair	438	18		5
801	30	≤10	23	101	58	185	Excellent	Good	445	20	174	>5
802	25	≤10	23	98	60	184			440	23		>5
803	25	≤10	21	99	55	152			465	20		>5
804	35	≤10	23	100	59	165			471	20		>5
805	35	≤10	22	105	60	198			450	22		>5

Example 2

[0088]

Table 9

	Wire No.	Maximum depth of corrosion (μm)	Corrosion weight loss (mg/cm²)				Wire drawability	Tensile strength (N/mm²)	Elongation (%)	Fatigue strength (N/mm²)	Number of bending sequences
			Erosion-corrosion test								
			I	II	III	IV					
	1001	400	51	330	164	535	Fair	488	11		2
	1002	≤10	29	205	72	445		340	16		>5
	1003						Poor				
Comparative example 1	1004	140	34	235	95	495		335	20	130	>5
	1005	250	39	258	112	500		398	22	142	>5
	1006	240	38	260	113	493		397	22	143	>5

[0089]

Table 10

Wire No.	Average grain size (μm)	Maximum depth of corrosion (μm)	Corrosion weight loss (mg/cm²) Erosion-corrosion test				Castability	Wire drawability	Tensile strength (N/mm²)	Elongation (%)	Fatigue strength (N/mm²)	Number of bending sequences
			I	II	III	IV						
2001	800	90	28	145	90	345	Fair	Poor	399	15	135	3
2002	700	90	27	153	80	320	Fair	Poor	405	16	138	3
2003	200	≤10	24	110	64	240	Good	Fair	425	20	162	5
2004	180	380	47	325	170	498			456	16	150	3
2005	350	480	55	350	203	566		Poor	478	11	148	2
2006	40	20	33	216	94	495			410	25	150	>5
2007	250	≤10	25	126	68	402			375	17	140	5
2008	350	≤10	26	168	75	456			335	15	133	4
2009	40						Poor	Poor				
2010	150							Poor				
2011	25											
2012	400						Poor					
2013	300	30	27	113	82	215	Fair	Poor	470	14	160	3
2501	1000	40	24	118	92	345	Fair	Fair	405	12	135	3
2502	1200						Poor					
2503	1300						Poor					
2504	1500						Poor					
2505	1500						Poor					

Comparative example 2

[0090]

Table 11

	Cultivation net No.	Wire No.	Cultured fish	Wire thickness loss (mm)			
				Corner in draft region	Periphery in draft region	Periphery	Bottom
Example 3	1	405	Yellowtail	0.44	0.36	0.09	0.57
			Salmon	0.42	0.35	0.03	0.05
	2	509	Yellowtail	0.39	0.34	0.08	0.53
			Salmon	0.38	0.33	0.03	0.05
	3	521	Yellowtail	0.36	0.3	0.06	0.49
			Salmon	0.34	0.29	0.02	0.04
	4	704	Yellowtail	0.37	0.32	0.07	0.45
			Salmon	0.36	0.32	0.03	0.05
Comparative example 3	5	1004	Yellowtail	0.8	0.62	0.25	1.35
			Salmon	0.85	0.64	0.08	0.1
	6	1005	Yellowtail	1.05	0.75	0.28	2.0
			Salmon	0.99	0.77	0.12	0.15